ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 2583–2585

www.rsc.org/chemcomm

COMMUNICATION

Magnetically recoverable SiO_2-coated Fe_3O_4 nanoparticles: a new platform for asymmetric transfer hydrogenation of aromatic ketones in aqueous medium†

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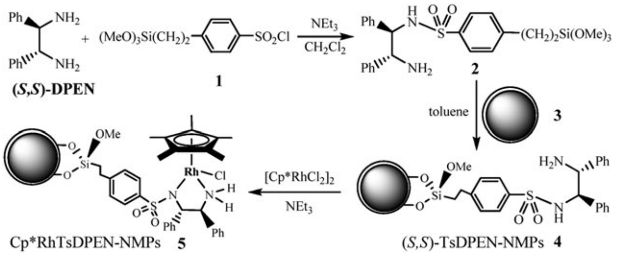
Received 8th September 2010, Accepted 29th November 2010
DOI: 10.1039/c0cc03730c

A magnetically recoverable chiral rhodium catalyst exhibited excellent catalytic activity and enantioselectivity in asymmetric transfer hydrogenation of aromatic ketones in aqueous medium, which could be recovered easily *via* a small magnet and used repetitively ten times without obviously affecting its enantioselectivity.

Asymmetric catalysis in environmentally friendly processes represents an important branch of green chemistry, which can greatly reduce pollution.[1] Learning from enzyme catalysis in biochemical processes, most studies are focused on homogeneous chiral catalysts. For example, chiral η^5-Cp*–M (M = Ru, Rh and Ir) complexes bearing *N*-sulfonylated 1,2-diamines have been widely used in asymmetric hydrogenation of ketones[2] and some of them can significantly accelerate asymmetric transfer hydrogenation of ketones in aqueous medium.[3] However, their practical applications are still hindered due to difficulties in separation and reuse, leading to a high cost and even a heavy pollution from metallic ions. Although immobilized homogeneous catalysts on general polymer or inorganic materials[4] have exhibited obvious advantages of easy separation and efficient recycling, most catalysts still suffer from lower catalytic efficiencies than corresponding homogeneous catalysts owing to uncontrollable hindrance and changes in the chiral microenvironment of active sites. Previously, we reported a series of heterogeneous catalysts anchored on ordered silica supports,[5] some of them had exhibited excellent enantioselectivities in asymmetric catalysis because of ordered mesoporous channels and good compatibility of surface functionalities. However, the irregular shape with long pore channels of silica supports will inevitably decrease the catalytic efficiencies and also add a problem in catalyst separation. Thus, based on highly catalytic efficiency, giving consideration to highly efficient recycling of catalyst has attracting extensive research interest.

Directly anchoring homogeneous chiral catalysts on magnetic nanoparticles can provide a more convenient strategy to tailor the uniform shape of catalysts, making recovery and reuse much easier *via* an suitable external magnetic field.[6–8] More importantly, immobilization of a homogeneous chiral catalyst on the outside surface of a rigid nanoparticle can keep the same chiral microenvironment as a homogeneous catalyst and can maintain excellent stereocontrol performance. However, potential magnetic aggregation of bare magnetic nanoparticles[7] and magnetic loss of magnetic mesocellular[8] are still challenges for practical application. Herein, we develop a convenient method for preparing a magnetically recoverable chiral rhodium catalyst through direct complexation of $[Cp^*RhCl_2]_2$ with (*S*,*S*)-TsDPEN-modified SiO_2-coated Fe_3O_4 nanoparticles, and apply it to asymmetric transfer hydrogenation of aromatic ketones in aqueous medium. The key feature is that this SiO_2-coated magnetic nanoparticle can not only act as a new platform to anchor different types of chiral catalysts for asymmetric catalysis but also can greatly improve dispersibility of active species to decrease aggregation of active catalysts. In particular, the tailored structure and surface chemistry of SiO_2-coated magnetic nanoparticles are a benefit to build an analogously homogeneous chiral microenvironment and to keep an excellent catalytic efficiency.

The chiral rhodium catalyst anchored on the magnetic nanoparticles, denoted as Cp*-Rh-TsDPEN-MNPs (**5**), was prepared according to the procedures illustrated in Scheme 1. Firstly, the SiO_2-coated Fe_3O_4 magnetic nanoparticles (**3**) with *ca.* 400 nm average diameter were synthesized readily *via* a similar reported solvothermal method,[9] followed by a SiO_2-coated procedure.[10] (*S*,*S*)-TsDPEN-derived ligand **2**[11] was then grafted onto the magnetic nanoparticles. Finally,



Scheme 1 Preparations of the catalyst **5**.

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† Electronic Supplementary Information (ESI) available: [Experimental procedures and analytical data for obtained chiral alcohols]. See http://dx.doi.org/10.1039/c0cc03730c/

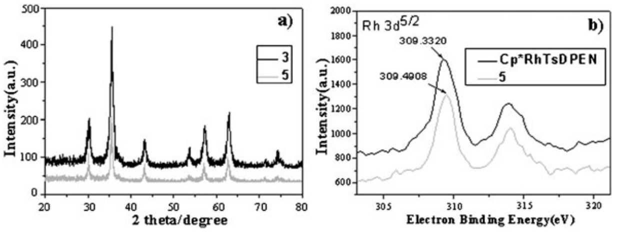
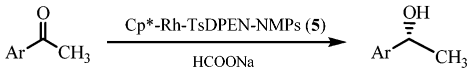


Fig. 1 (a) Wide-angle powder XRD patterns of **3** and **5**. (b) XPS spectra of Cp*RhTsDPEN and **5**.

Table 1 Asymmetric transfer hydrogenation of aromatic ketones[a]



Entry	Ar	Catalyst	Conv. (%)[b]	ee (%)[b]
1	Ph	**5**	97.2	97.7
2	Ph	Cp*RhTsDPEN	98.5[c]	97.3[c]
3	Ph	**4** + $[Cp^*RhCl_2]_2$	86.1	84.0
4	Ph	**3** + Cp*RhTsDPEN	80.3	96.1
5	4-ClPh	**5**	99.2	93.2
6	4-FPh	**5**	97.8	92.4
7	4-MePh	**5**	97.6	92.4
8	4-OMePh	**5**	97.8	90.8
9	2-Naphthyl	**5**	99.8	90.1

[a] Reaction conditions: catalysts (4.0 μmol of Rh, based on the ICP analysis), HCO_2Na (0.68 g, 10.0 mmol), Bu_4NBr (0.29 g, 0.80 mmol), ketone (2.0 mmol) and 2.0 mL water, reaction temperature (40 °C), reaction time (1.0 h). [b] Determined by chiral GC or HPLC analysis (Fig. S3). [c] Data were obtained using the homogeneous catalyst.

the catalyst **5** was successfully obtained as a brown powder *via* directly complexing **4** with $[Cp^*RhCl_2]_2$ using NEt_3 as a basic reagent (see ESI†). The inductively coupled plasma (ICP) optical emission spectrometer analysis showed that the Rh loading amount in the catalyst **5** was 16.92 mg (0.164 mmol) per gram of catalyst, which was consistent with the 1 : 2 mole ratio of Rh to N atom confirmed by elemental analysis that calculated a mass % of N (0.46%) with 0.329 mmol content.

Wide-angle XRD patterns (Fig. 1a) showed that, after being immobilized with rhodium complex, the typical diffraction peaks indicative of Fe_3O_4 were still clearly observed,[12] suggesting that the surface modification had no significant effect on the nature of Fe_3O_4. An FT-IR spectrum of the catalyst **5** (Fig. S1†) demonstrated successful incorporation of them onto the magnetic nanoparticles, in which relatively weak absorption bands around 3100–2800 cm^{-1} for ν(C–H) and 1594–1445 cm^{-1} for ν(C=C) were derived from the organometallic rhodium complex.[13] Scanning electron microscopy (SEM) revealed that the catalyst **5** presented the uniform size of nanoparticles with average diameter around 400 nm (Fig. 2a). Transmission electron microscopy (TEM) further confirmed that this core–shell catalyst **5** was encapsulated by a thin silica layer of ~30 nm in thickness (Fig. 2b). The magnetization curves (Fig. 2c) showed that **3** and catalyst **5** were superparamagnetic and had the magnetization saturation values of 132.8 and 58.9 emu g^{-1}, in which catalyst **5** was readily dispersible in the reaction system and could be easily separated with a small magnet near the bottle (Fig. 2d).

Table 1 summarizes catalytic performances in asymmetric transfer hydrogenation of aromatic ketones. In general, high conversions and high enantioselectivities were obtained for all tested aromatic ketones. Taking acetophenone as an example (entry 1), it was found that 97.2% conversion and 97.7% ee value of (*S*)-1-phenyl-1-ethanol were obtained with 1 h reaction time, which was comparable to that of the parent catalyst (entry 1 *versus* entry 2). The high catalytic activity of the catalyst **5** could be attributed to the high dispersion of rhodium active sites onto the outer surface of the SiO_2-coated Fe_3O_4 nanoparticles. While, the high enantioselectivity confirmed that the homogeneous microenvironment could be preserved after being immobilized. This behaviour was proved by the XPS spectra (Fig. 1b), in which the same binding energies of catalyst **5** as Cp*RhTsDPEN[3a] and an obvious difference from $[Cp^*RhCl_2]_2$ were observed (Fig. S2†).

To gain better insight into the nature of catalyst **5** and to eliminate the non-covalent adsorption on catalytic process, two control experiments were carried out using **4** plus $[Cp^*RhCl_2]_2$ and **3** plus Cp*RhTsDPEN as chiral catalysts. It was found that the former afforded the corresponding alcohol with 86.1% conversion and 84.0% ee value (entry 3), while the latter gave the corresponding alcohol with 80.3% conversion and 96.1% ee value (entry 4). The former suggested that the catalyst synthesized by an *in situ* postmodification method could result in a medium catalytic performance. Lower catalytic activity and enantioselectivity than catalyst **5** may be due to the fact that the small part of $[Cp^*RhCl_2]_2$ had not been coordinated on the catalytic process, in which the part of loss of Rh was detected by ICP analysis in solution. The latter indicated that the chiral microenvironment had not been changed from non-covalent adsorption. Low conversion suggested that part of the catalyst did not participate in the catalytic reaction due to the jam from physical absorption. Complete disappearance of activity and enantioselectivity indicated that the non-covalent adsorption in the catalytic process could be eliminated when employing the catalyst after Soxhlet extraction (**3** plus Cp*RhTsDPEN). This deduction was proved by ICP analysis (nearly the same loading amount of Rh was detected in solution after Soxhlet extraction).

An important feature of the heterogeneous catalyst **5** is that it is convenient to recover and recycle. As shown in Fig. 2d, the catalyst **5** was quantitatively recovered *via* a small magnet. Meanwhile, in ten consecutive reactions the recycling of catalyst **5** still afforded 91.9% conversion and 92.5% ee value using acetophenone as a substrate (Fig. 3).

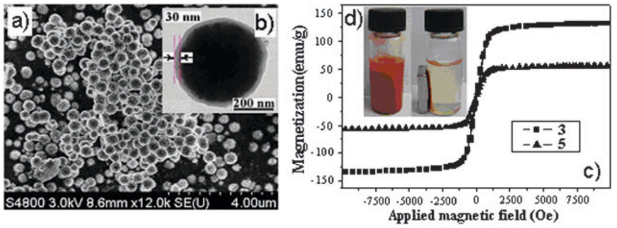


Fig. 2 (a) SEM image, (b) TEM image and (c) magnetization curves of **3** and the catalyst **5** measured at 300 K. (d) The separation–redispersion process of the catalyst **5**.

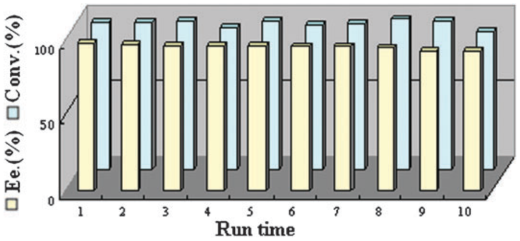


Fig. 3 Reusability of **5** using acetophenone as a substrate.

In conclusion, we supplied a facile approach to prepare a magnetically recoverable rhodium catalyst, which exhibited excellent catalytic activities (up to 99%) and enantioselectivities (up to 97% ee) in the asymmetric transfer hydrogenation of aromatic ketones. In particular, the heterogeneous catalyst could be recovered easily by using a magnet, in which neither filtration nor extraction was necessary. The recycling catalyst (reused 10 times) still showed high catalytic efficiency without obviously affecting its enantioselectivity, showing good potential for industrial application.

We are grateful to China National Natural Science Foundation (20673072), Shanghai Sciences and Technologies Development Fund (10dj1400103 and 10jc1412300) and Shanghai Municipal Education Commission (08YZ71 and S30406) for financial support.

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